

EXPRESS MAIL LABEL NO. EV013298336US

JG07 Rec'd PCT/PTO 18 MAR 2007

Form PTO-1390 (REV 11-98)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 480821.90116
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			US. APPLICATION NO. (If known, see 37 CFR 1.5) 10/088403
INTERNATIONAL APPLICATION NO. PCT/GB00/03603	INTERNATIONAL FILING DATE 20 Sept 2000 (20.09.00)	PRIORITY DATE CLAIMED 20 Sept 1999 (20.09.99)	
TITLE OF INVENTION PHOTONIC CRYSTAL MATERIALS			
APPLICANT(S) FOR DO/EO/US TURBERFIELD, Andrew Jonathan; DENNING, Robert Gordon			
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input checked="" type="checkbox"/> has been transmitted by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input checked="" type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11. to 16. below concern document(s) or information included:</p> <ol style="list-style-type: none"> <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98 and Form 1449. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input checked="" type="checkbox"/> Other items or information: Copy of Form PCT/IB/308 dated 29 March 2001 Confirming Transmittal of the International Application to the US as Designated Office; Postcard 			

U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5) <div style="font-size: 1.5em; font-weight: bold;">10/088403</div>		INTERNATIONAL APPLICATION NO. PCT/GB00/03603		ATTORNEY'S DOCKET NUMBER 480821.90116	
17. [X] The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 <div style="text-align: right;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div>				CALCULATIONS PTO USE ONLY <div style="border: 1px solid black; padding: 2px;">\$890.00</div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				<div style="border: 1px solid black; padding: 2px;">\$</div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	23 -20 =	3	X \$18.00	\$ 54.00	
Independent claims	1 -3 =	0	X \$78.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable) -			+ \$260.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$944.00	
[X] Applicant hereby claims small entity status. Reduction by 1/2 for filing by small entity.				\$472.00	
SUBTOTAL =				\$472.00	
Processing fee of \$130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.429(f)).				+ \$	
TOTAL NATIONAL FEE =				\$472.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				+ \$	
TOTAL FEES ENCLOSED =				\$420.00	
				Amount to be: refunded	\$
				Charged	\$
a. [] A check in the amount of \$ <u> . 00 </u> to cover the above fees is enclosed. b. [X] Please charge my Deposit Account No. <u>17-0055</u> in the amount of <u>\$472.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed. c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>17-0055</u> . A duplicate copy of this sheet is enclosed. NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status. <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> SEND ALL CORRESPONDENCE TO: Quarles & Brady LLP 411 East Wisconsin Ave. Milwaukee, WI 53202-4497 </div> <div style="width: 45%; text-align: center;"> <div style="font-size: 1.2em; font-family: cursive;">Jean C. Baker</div> <div style="border-top: 1px solid black; width: 100%; margin: 2px 0;"></div> SIGNATURE <div style="border-top: 1px solid black; width: 100%; margin: 2px 0;"></div> NAME <div style="border-top: 1px solid black; width: 100%; margin: 2px 0;"></div> 35,433 REGISTRATION NUMBER </div> </div>					

10088403 111102

10,088403

JC10 Rec'd PCT/PTO 18 MAR 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: **TURBERFIELD**

Docket No.: 480821.90116

Serial No.: **Unassigned**

Filed: **Concurrently herewith**

Int'l appln No.: **PCT/GB00/03603**

Int'l filing date: **20 Sept 2000**

Title: **PHOTONIC CRYSTAL MATERIALS**

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

In connection with the above-identified application filed herewith, please enter the following preliminary amendment:

IN THE CLAIMS:

The claims have been amended to read as follows. A copy of the marked claims showing the amendments made is attached.

1. A method of forming a photonic crystal material comprising exposing a photosensitive material to an interference pattern of electromagnetic radiation whereby the exposure through the material varies in accordance with the spatially varying intensity created by the interference to produce a three dimensional periodic variation in the refractive index of the photosensitive material based on the exposure, the photosensitive material possessing an average number of crosslinkable groups per molecule of at least 3 with an equivalent weight per crosslinkable group of at most 1000.
2. A method according to claim 1, wherein the irradiated sample of photosensitive material is developed to remove less irradiated regions of the sample.

3. A method according to claim 1 wherein the photosensitive material is an epoxy resin.
4. A method according to claim 1 wherein the number of crosslinkable groups per molecule is at least 6.
5. A method according to claim 4 wherein the number of crosslinkable groups per molecule is about 8.
6. A method according to claim 1 wherein the equivalent weight per crosslinkable group is at most 300.
7. A method according to claim 6 wherein the equivalent weight per crosslinkable group is at most 230.
8. A method according to claim 1 wherein the photosensitive materials is a glycidyl ether of bisphenol A novolac resin.
9. A method according to claim 8 wherein the resin is one where the number of epoxy groups per molecule is about 8 and the resin is co-polymerised with a less crosslinkable plasticising epoxy monomer.
10. A method according to claim 1 wherein the photosensitive material comprises a photoacid generator.
11. A method according to claim 10 wherein the photoacid generator possesses a molar extinction coefficient of 50 to 2000 mol⁻¹ dm³ cm⁻¹ at the wavelength of radiation being used, is used at a concentration at which it does not absorb more than 5% of the radiation which is incident upon it while having a quantum efficiency which is sufficient for the exposure to cause insolubilisation of the photosensitive material.

12. A method according to claim 11 wherein the molar extinction coefficient is 100 to 500 mol⁻¹ dm³ cm⁻¹.
13. A method according to claim 11 wherein the photoacid generator is a triaryl sulphonium salt.
14. A method according to claim 1 wherein the photosensitive material is cured by subsequent heating to cause acid catalysed polymerisation.
15. A method according to claim 14 wherein the photosensitive material is cured by heating at 40°C to 120°C for 1 to 20 minutes.
16. A method according to claim 14 wherein the heating is carried out at a temperature below the melting point of the photosensitive material.
17. A method according to claim 2 wherein material is introduced into the voids produced by development of the irradiated photosensitive material.
18. A method according to claim 17 wherein the optical properties of the irradiated sample are adjusted by the introduction of a material having a predetermined refractive index that is different from that of the irradiated photosensitive material.
19. A method according to claim 17 wherein the irradiated sample is used as a template for the production of other composite materials having periodic variations in refractive index.
20. A method according to claim 1, wherein the photosensitive material is subjected to multiple exposures, each exposure producing respective interference patterns.

10,088403

JC10 Rec'd PCT/PTO 1 8 MAR 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: **CHANDRASEKAR** Docket No.: 410718.90116
Serial No.: **Unassigned** Filed: **Concurrently herewith**
Int'l appln No.: **PCT/CA00/01132** Int'l filing date: **21 Sept 2000**
Title: **LOCAL DELIVERY OF 17-BETA ESTRADIOL FOR
PREVENTING VASCULAR INTIMA HYPERPLASIA AND FOR
IMPROVING VASCULAR ENDOTHELIUM FUNCTION AFTER
VASCULAR INJURY**

CLAIM SET SHOWING AMENDMENTS MADE

1. The use of 17- β estradiol or a derivative thereof in the making of a medication or a device for in-situ administration in the lumen of a blood vessel having suffered vascular injury, at the injured site, for improving reendothelization and vascular endothelial function in a patient.
2. The use as defined in claim 1, wherein 17- β estradiol or a derivative thereof is present in a dose unit of 1 to 5000 $\mu\text{g/Kg}$ of patient's body weight.
3. The use, as defined in claim 1, wherein 17- β estradiol or a derivative thereof is present in a dose unit of 10 to 50 $\mu\text{g/Kg}$ of patient's body weight.
4. The use as defined in claim 1, wherein 17- β estradiol or a derivative thereof is present in a dose unit of 10 to 30 $\mu\text{g/Kg}$ of patient's body weight.
5. The use as defined in [any one of claims 1 to 5] claim 1, wherein said pharmaceutically acceptable carrier comprises hydroxypropyl-beta-cyclodextrin (HPCD).

6. A method according to [any one of the preceding claims] claim 1 wherein the equivalent weight per crosslinkable group is at most 300.
7. A method according to claim 6 wherein the equivalent weight per crosslinkable group is at most 230.
8. A method according to [any one of the preceding claims] claim 1 wherein the photosensitive materials is a glycidyl ether of bisphenol A novolac resin.
9. A method according to claim 8 wherein the resin is one where the number of epoxy groups per molecule is about 8 and the resin is co-polymerised with a less crosslinkable plasticising epoxy monomer.
10. A method according to [any one of the preceding claims] claim 1 wherein the photosensitive material comprises a photoacid generator.
11. A method according to claim 10 wherein the photoacid generator possesses a molar extinction coefficient of 50 to 2000 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ at the wavelength of radiation being used, is used at a concentration at which it does not absorb more than 5% of the radiation which is incident upon it while having a quantum efficiency which is sufficient for the exposure to cause insolubilisation of the photosensitive material.
12. A method according to claim 11 wherein the molar extinction coefficient is 100 to 500 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$.
13. A method according to claim 11 [or 12] wherein the photoacid generator is a triaryl sulphonium salt.
14. A method according to [any one of the preceding claims] claim 1 wherein the photosensitive material is cured by subsequent heating to cause acid catalysed polymerisation.

15. A method according to claim 14 wherein the photosensitive material is cured by heating at 40°C to 120°C for 1 to 20 minutes.

16. A method according to claim 14 [or 15] wherein the heating is carried out at a temperature below the melting point of the photosensitive material.

17. A method according to [any one of the preceding claims] claim 2 wherein material is introduced into the voids produced by development of the irradiated photosensitive material.

18. A method according to claim 17 wherein the optical properties of the irradiated sample are adjusted by the introduction of a material having a predetermined refractive index that is different from that of the irradiated photosensitive material.

19. A method according to claim 17 wherein the irradiated sample is used as a template for the production of other composite materials having periodic variations in refractive index.

20. A method according to [any one of the preceding claims] claim 1, wherein the photosensitive material is subjected to multiple exposures, each exposure producing respective interference patterns.

21. A method according to [any one of the preceding claims] claim 1, wherein the three dimensional pattern is formed by directing electromagnetic radiation from at least four beams at the photosensitive material so as to intersect and interfere within it.

22. A method according to claim 1 substantially as hereinbefore described.

23. A photonic crystal material wherever formed by a method as claimed in [any one of the preceding claims] claim 1.

PHOTONIC CRYSTAL MATERIALS

5 This invention relates to photonic crystal materials and a method for their preparation.

10 In our WO99/09439 we describe a photonic crystal material that has a 3-D periodic structure with a periodicity that varies on a length scale comparable to the wavelength of electromagnetic radiation. The 3-D periodic structure is produced by irradiating photosensitive material with electromagnetic radiation such that interference between radiation propagating in different directions within the sample gives rise to a 3-D periodic variation in intensity within the sample. Thereafter the irradiated material is developed to remove the less or more irradiated regions of the material to produce a structure having 3-D periodicity in the refractive index of the composite material (because irradiation produces a change in the refractive index). In general, the less irradiated regions are subsequently removed leaving voids which can, if desired, be filled, for example with material having a refractive index which is different from that of the irradiated photosensitive material. If desired, the irradiated sample can be used as a template for the production of other materials having periodic variations in refractive index.

20 The present invention relates to an improved process for the production of such photonic crystal materials.

25 In particular, it has now been found that improved results can be obtained by using a photosensitive material with a high degree of functionality. According to the present invention there is provided a method forming a photonic crystal material comprising exposing a photosensitive material to an interference pattern of electromagnetic radiation whereby the exposure through the material varies in accordance with the spatially varying intensity created by the interference to produce a three dimensional periodic variation in the refractive index of the

30

photosensitive material based on the exposure, the photosensitive material possessing an average number of crosslinkable groups per molecule of at least 3 or 3.5 with an equivalent weight per crosslinkable group of at most 1000. It has been found that with high functionality the network of crosslinks formed is potentially very dense giving high solubility contrast between strongly and weakly exposed material.

In general the photosensitive materials used in this invention are those possessing an average number of crosslinkable groups per molecule of at least 4, preferably at least 6 and especially about 8. They have an equivalent weight per crosslinkable group (XEW) in general at most 500, typically at most 400, preferably at most 300, especially at most 230. Suitable photosensitive materials which can be used include epoxy resins ie. epoxy groups act as the crosslinkable groups.

It has been found that it is particularly advantageous to use the glycidyl ether of bisphenol A novolac which is available as EPON-SU-8 from Shell Chemicals. This resin has low intrinsic absorption at the laser wavelength ($\lambda = 355$ nm) and is capable of sub-0.1 micron resolution. It has an average of 8 epoxy groups per molecule. The material is therefore mostly in the form of a tetramer although other oligomers will usually be present. Its XEW is generally about 215, with a typical range from 190 to 230. It may be desirable to co-polymerise this material with a less crosslinkable plasticising epoxy monomer e.g. one with a single epoxy group in order to minimise shrinkage and/or film distortion on heating of the material (thereby reducing the functionality somewhat). Alternatively, the resin can be modified by using a so-called "expanding" monomer such as a spiro-orthocarbonate. Alternatively, improved physical properties of the polymer can be obtained by the addition of a binding agent such as a linear polymer. Effectively, any polymer can be used provided that it has sufficiently high functionality and the precursors have a low degree of optical absorption at the laser wavelength within a film typically 10-100 microns thick.

In one preferred embodiment of the present invention the photosensitive material is subjected to irradiation in the presence of a photoacid generator. Subsequent to exposure the material is heated to cure the crosslinked material.

5 Suitable photoacid generators (PAG) which can be used, especially with epoxy resins, include onium salts such as triaryl sulfonium salts including triphenyl sulfonium antimony chloride which is available as Cyracure UV1 from Union Carbide. This particular generator is well suited to irradiation at 355 nm where it has sufficient absorption

10 (molar extinction coefficient $\sim 300 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). In general the molar extinction coefficient of the PAG should be from $50 - 2000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ at the laser wavelength. If the molecular coefficient is too large, the requirement for the sample to be optically thin means that the concentration of initiators is too small to effect polymerisation. On the other hand if it is too small, the PAG

15 concentration is so high that it adversely affects the properties of the polymer. By "optically thin" is meant that at the concentration at which it is used the PAG does not absorb more than 5% of the radiation which is incident upon it. In addition the quantum efficiency of the PAG should be sufficient for the exposure to cause insolubilisation of the photosensitive material. The effective quantum

20 efficiency will be enhanced if the system involves chemical amplification. Obviously sufficient photosensitive material must be insolubilised to provide a volume of insolubilised material which is useful for practical purposes i.e. a useful volume, for example 1 mm^3 e.g. a film of size $5 \times 5 \times 0.04 \text{ mm}$. By "cause insolubilisation" is meant that there is sufficient proton generation for subsequent

25 acid catalysed polymerisation, as discussed below, to result in a crosslinked material which is insoluble in a solvent which dissolves the unirradiated or weakly irradiated material. One of skill in the art will, of course, be able to select an appropriate PAG from those possessing the required molar extinction coefficients and optical thinness. For SU-8 a quantum efficiency of about 0.2 is needed for

30 proton generation in the PAG. It is believed that the insolubility threshold is reached when each absorbed photon leads to the conversion of material equivalent

to about 250 or 500 crosslinkable groups, for example about 600 epoxy groups, into insoluble polymer.

It will be appreciated that if a photonic crystal is to be prepared using a different wavelength source then a different PAG will generally be needed. One of skill in the art will be able to select an appropriate PAG given the literature on this subject for microlithography. Alternatively, the addition of a sensitizer which is not in itself absorbing generally renders the PAG effective for longer wavelengths. For shorter wavelengths other triaryl sulfonium salts or diaryl-iodonium salts can generally be used.

It is a further feature of the present invention that the subsequent curing or baking of the exposed material is carried out at a temperature below the melting of the precursor in order to suppress proton diffusion and thus maintain a fidelity with the intensity pattern. This contrasts with the conditions used in conventional lithography for semi-conductor fabrication. It will be appreciated that the exposure to light results in the production of a proton from the photochemically induced fragmentation of the PAG molecule. Acid catalysed polymerisation of the resin occurs at the post-exposure bake. The precise temperature and time will depend on the exposure dose, the concentration of PAG in the resist and the required filling factor. Typically, though, the bake will take place at 40 to 120°C for, say, 1 to 20 minutes. Since the melting point of the SU-8 resin is 80 to 90°C, the temperature should be kept below this in order that a much "cleaner" lattice is produced.

In effect, therefore, exposure produces a latent image which is realised on subsequent baking. In view of this latency it is possible to employ multiple exposures, well separated in time. This can be used, for example, to superimpose two different periodicities or to write specific defect or waveguide structures into the material, before or after the principal exposure.

In order to prepare a film of the photoresist material, it is first dissolved in

a suitable solvent. The solution is typically spun onto a fused silica disk.

Alternatively the film can be prepared by, for example, spreading, moulding or pouring. For EPON-SU-8 a suitable solvent is γ -butyrolactone, typically at 50 to 60% weight resist concentration, which can be obtained with gentle heating (~30 to 40°C) and manual stirring, with the resulting viscous solution filtered to exclude particles larger than, say 1 μ m. Typically the 50% weight resist can be used to give rise to a film from 2 to 30 microns thick while the 60% material will give a thickness of 10 to 60 microns. The solution also contains the PAG, typically at a concentration of 0.5 to 3%, generally from 1.0 to 2.0%, by weight. The amount of PAG added determines the sensitivity; with this particular combination about 1.2% concentration gives good results. The photosensitive material can be stored in the dark away from the heat sources until required.

Approximately 2 ml of the solution can be pipetted onto a disk, typically of fused silica, of about 2 cm diameter so that it is flooded, to prepare a film of about 30 μ m. The film is then spun at, typically 1000 rpm (5s ramp up, 40s hold, 5s ramp down). The material is then heated to evaporate the solvent, typically at 50°C for 5 minutes and followed by 15 minutes at 90-100°C. The interval between film preparation and exposure should be kept as short as possible and generally less than 30 minutes.

The film is then exposed to an interference pattern created at the intersection of four beams from a frequency-tripled, injection seeded, Q-switched Nd:Yag laser (wavelength $\lambda = 355$ nm). Such a pattern has three-dimensional translational symmetry.

The propagation directions, polarisation directions and relative intensities used are defined as follows

Normalised optical wave-vectors, relative to the conventional fcc unit cells axes:

The pulse duration is not critical. With an injection seeded laser the coherence length is equal to the pulse length, but this requirement can be relaxed if the optical path-lengths are made accurately equal. A cheaper but less effective option for increasing the coherence length is etalon-narrowing. In practice it is only necessary to achieve a coherence length of $\sim 1\text{cm}$. An ordinary un-narrowed

Q-Switched Nd-YAG laser can approach this requirement. More importantly though injection-seeding makes the pulse energies, following third harmonic generation, far more reproducible, so that the control of the dose in a single pulse exposure becomes straightforward. Typically electromagnetic radiation is directed at the sample from at least four beams so as to intersect and interfere within it.

Alternative lasers can be used, providing the photo initiator is chosen to match the operating wavelength. An optical parametric oscillator which is continuously tunable, could therefore be used to construct crystals with different interference patterns with or without a change in the angles between the interfering beams. The main advantage of single pulse operation is the absence of significant refractive index changes, that could perturb the interference, during the exposure.

After exposure the film is baked to cure the resin. This can be achieved by placing the glass substrate on a level hotplate at 40-120°C for 1-20 minutes. The film is then developed to dissolve away the uncrosslinked resin. For the epoxy resin SU-8 this can be achieved by using propyl glycol methyl ether acetate (PGMEA). Typically the substrate with the attached film is placed in a container with the solvent in an ultrasonic bath until the film becomes detached. The power is damped or attenuated to ~7W to avoid mechanical damage to the film as it releases from the substrate. Typically this is achieved at a temperature of 40 to 50°C for, say, 40 minutes for a 30 micron film. After this the film is washed with fresh PGMEA and then rinsed before drying. For this purpose an alcohol such as isopropyl alcohol can be used. In this way we have prepared photonic crystal films with thicknesses from 10 to 80 μm (e.g. 10 to 30 μm), corresponding to 14 to 84 (e.g. 14 to 42) close-packed layers.

All other features of the method described in WO99/09439, to which reference should be made, can be used. For example the photosensitive material can be subjected to multiple exposures, each exposure producing respective

interference patterns.

The accompanying Figure shows a scanning electron micrograph (SEM) of a polymeric microstructure produced by exposure to the interference pattern
5 created at the intersection of four beams from a frequency-tripled injection seeded, Q-switched Nd:Yag laser of a $10\mu\text{m}$ film of photoresist based on Epon-SU8. The scale bar is $10\mu\text{m}$. Refraction at the film surface changes the incident wavevectors, stretching the interference pattern in the $[111]$ direction. During processing film shrinkage of 10-20% occurs. The developed film is hard and brittle; its top surface
10 is a (111) plane and it has been fractured to reveal $(11\bar{1})$ cleavage planes.

CLAIMS

1. A method of forming a photonic crystal material comprising exposing a photosensitive material to an interference pattern of electromagnetic radiation
5 whereby the exposure through the material varies in accordance with the spatially varying intensity created by the interference to produce a three dimensional periodic variation in the refractive index of the photosensitive material based on the exposure, the photosensitive material possessing an average number of crosslinkable groups per molecule of at least 3 with an equivalent weight per crosslinkable group of at most
10 1000.
2. A method according to claim 1, wherein the irradiated sample of photosensitive material is developed to remove less irradiated regions of the sample.
3. A method according to claim 1 or 2 wherein the photosensitive material is an epoxy resin.
- 15 4. A method according to any one of claims 1 to 3 wherein the number of crosslinkable groups per molecule is at least 6.
5. A method according to claim 4 wherein the number of crosslinkable groups per molecule is about 8.
6. A method according to any one of the preceding claims wherein the
20 equivalent weight per crosslinkable group is at most 300.
7. A method according to claim 6 wherein the equivalent weight per crosslinkable group is at most 230.
8. A method according to any one of the preceding claims wherein the photosensitive material is a glycidyl ether of bisphenol A novolac resin.
- 25 9. A method according to claim 8 wherein the resin is one where the number of epoxy groups per molecule is about 8 and the resin is co-polymerised with a less crosslinkable plasticising epoxy monomer.
10. A method according to any one of the preceding claims wherein the photosensitive material comprises a photoacid generator.
- 30 11. A method according to claim 10 wherein the photoacid generator possesses a molar extinction coefficient of 50 to 2000 mol⁻¹ dm³ cm⁻¹ at the

wavelength of radiation being used, is used at a concentration at which it does not absorb more than 5% of the radiation which is incident upon it while having a quantum efficiency which is sufficient for the exposure to cause insolubilisation of the photosensitive material.

- 5 12. A method according to claim 11 wherein the molar extinction coefficient is 100 to 500 mol⁻¹ dm³ cm⁻¹.
13. A method according to claim 11 or 12 wherein the photoacid generator is a triaryl sulphonium salt.
14. A method according to any one of the preceding claims wherein the
10 photosensitive material is cured by subsequent heating to cause acid catalysed polymerisation.
15. A method according to claim 14 wherein the photosensitive material is cured by heating at 40°C to 120°C for 1 to 20 minutes.
16. A method according to claim 14 or 15 wherein the heating is carried
15 out at a temperature below the melting point of the photosensitive material.
17. A method according to any one of the preceding claims wherein material is introduced into the voids produced by development of the irradiated photosensitive material.
18. A method according to claim 17 wherein the optical properties of the
20 irradiated sample are adjusted by the introduction of a material having a predetermined refractive index that is different from that of the irradiated photosensitive material.
19. A method according to claim 17 wherein the irradiated sample is used
25 as a template for the production of other composite materials having periodic variations in refractive index.
20. A method according to any one of the preceding claims, wherein the photosensitive material is subjected to multiple exposures, each exposure producing respective interference patterns.
21. A method according to any one of the preceding claims, wherein the
30 three dimensional pattern is formed by directing electromagnetic radiation from at least four beams at the photosensitive material so as to intersect and interfere within

it.

22. A method according to claim 1 substantially as hereinbefore described.

23. A photonic crystal material wherever formed by a method as claimed
5 in any one of the preceding claims.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
29 March 2001 (29.03.2001)

PCT

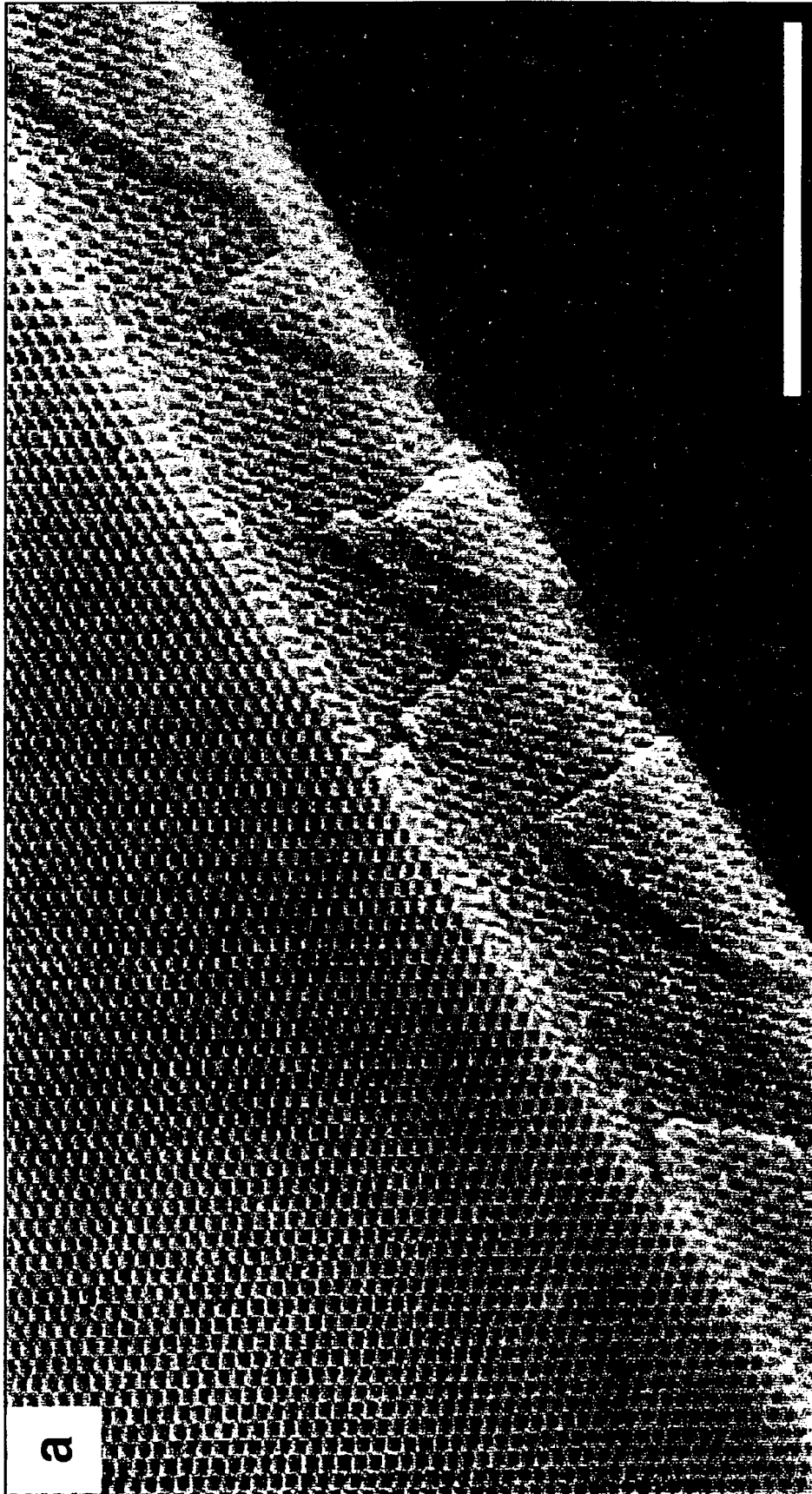
(10) International Publication Number
WO 01/22133 A1

- (51) International Patent Classification⁷: **G02B 6/12, C08L 63/00**
- (21) International Application Number: **PCT/GB00/03603**
- (22) International Filing Date:
20 September 2000 (20.09.2000)
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:
9922196.2 20 September 1999 (20.09.1999) **GB**
- (71) Applicant (for all designated States except US): **ISIS INNOVATION LIMITED [GB/GB];** Ewert House, Ewert Place, Summertown, Oxford OX2 7BZ (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **TURBERFIELD, Andrew, Jonathan [GB/GB];** 29 Derwent Avenue, Headington, Oxfordshire OX3 0AR (GB). **DENNING, Robert, Gordon [GB/GB];** 26 The Row, Tootbaldon, Oxfordshire OX44 9NE (GB).
- (74) Agent: **ELLIS-JONES, Patrick, George, Armine; J.A. Kemp & Co.,** 14 South Square, Gray's Inn, London WC1R 5LX (GB).
- (81) Designated States (national): **AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.**
- (84) Designated States (regional): **ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).**
- Published:**
— *With international search report.*
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: **PHOTONIC CRYSTAL MATERIALS**

(57) Abstract: A method of forming a photonic crystal material is disclosed comprising exposing a photosensitive material to an interference pattern of electromagnetic radiation whereby the exposure through the material varies in accordance with the spatially varying intensity created by the interference to produce a three dimensional periodic variation in the refractive index of the photosensitive material based on the exposure, the photosensitive material possessing an average number of crosslinkable groups per molecule of at least 3, with an equivalent weight per crosslinkable group of at most 1000, e.g. a glycidyl ether of bisphenol A novolac resin, preferably a SU-8 negative photoresist.

WO 01/22133 A1



5005 VON 11 OCT 13 10:29
 70A88C 10

N.76945B

Attorney's Docket No.

RULE 63 (37 C.F.R. § 1.63)
DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

As below named inventor(s), I/we hereby declare that

This declaration is of the following type:

- ☐ original
 ☐ design
 ☐ supplemental
☒ national stage of PCT
☐ divisional
 ☐ continuation
 ☐ continuation-in-part

My/our residence, post office address and citizenship are as stated below next to my/our name.

I/we believe I/we am/are the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PHOTONIC CRYSTAL MATERIALS

the specification of which (check one)

- ☐ is attached hereto
☐ was filed on _____
 in the United States Patent and Trademark Office as Application Serial No. _____
 and was amended on _____ (if applicable)
☐ was described and claimed in PCT International Application No. PCT/GB00/03603
 filed on 20 Sep 2000
 and as amended under PCT Article 19 on _____ (if any)

I/we hereby state that I/we have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I/we acknowledge the duty to disclose information which is material to patent ability as defined in 37 C.F.R. § 1.56.

I/we hereby claim foreign priority benefits under 35 U.S.C § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate or under § 365(a) of any PCT International Application(s) which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate or PCT International Application having a filing date before that of the application on which priority is claimed:

COMBINED DECLARATION AND POWER OF ATTORNEY

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119

Application No.	Country	Filing Date	Priority Claimed	
			Yes	No
9922196.2 ✓	GB ✓	20 Sep 1999 ✓	X	
PCT/GB00/03603 ✓		20 Sep 2000 ✓		

I/we hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below:

UNITED STATES PROVISIONAL APPLICATION(S)

Application No.	Filing Date

I/we hereby claim the benefit under 35 U.S.C. § 120 of any United States Application(s) or § 365(c) of any PCT International Application(s) designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I/we acknowledge the duty to disclose information which is material to patent ability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national PCT international filing date of this application.

PRIOR UNITED STATES/PCT INTERNATIONAL APPLICATION(S)

Application No.	Filing Date	Status (patented, pending/abandoned)
PCT/GB00/03603 ✓	20 Sep 2000 ✓	

I/we hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith:

Quarles & Brady LLP, 411 East Wisconsin Avenue Milwaukee Wisconsin 53202-4497 United States of America

I/we hereby declare that all statements made herein of my/our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C § 1001 and that such willful false statements may jeopardise the validity of the application or any patent issued thereon.

Inventors Signature

AS Transfer

7th May 2002

Date _____

Andrew Jonathan TURBERFIELD.

the United Kingdom

the United Kingdom

29 Derwent Avenue Headington Oxfordshire OX3 0AR the United Kingdom ~~GB~~X

Inventors Signature

Signature

7th May 200

Date _____

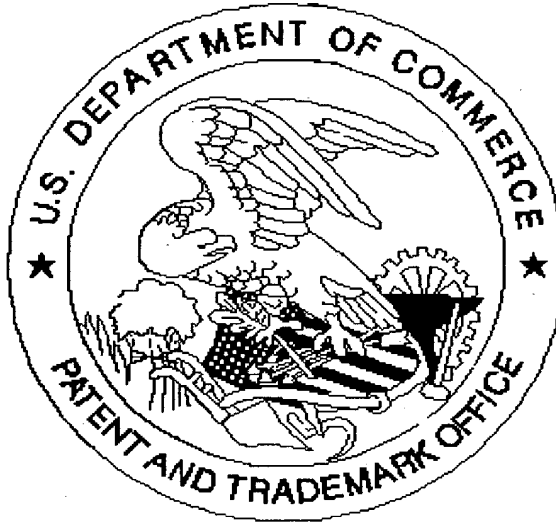
Robert Gordon DENNING

the United Kingdom

the United Kingdom

26 The Row Toothaldon Oxfordshire OX44 9NE GBX
the United Kingdom

United States Patent & Trademark Office
Office of Initial Patent Examination -- Scanning Division



Application deficiencies found during scanning:

☐ Page(s) _____ of _____ were not present
for scanning. (Document title)

☐ Page(s) _____ of _____ were not
present
for scanning. (Document title)

Scanned copy is best available. Figure is dark.